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Research paper

Ultrafast activation efficiency of three peroxides by $Fe_{78}Si_9B_{13}$ metallic glass under photo-enhanced catalytic oxidation: A comparative study

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A B S T R A C T

Metallic glasses with long-range disordered atomic structure have recently been attracted a great deal of research attention in catalytic field. Compared to crystalline materials, the metallic glasses present many advanced catalytic properties, yet the catalytic mechanism is not sufficiently understood. In this work, an $Fe_{78}Si_9B_{13}$ glassy ribbon manufactured by melt-spinning method was applied for the first time to compare its activation behavior on three peroxides, including hydrogen peroxide (H_2O_2), persulfate (PS) and peroxymonosulfate (PMS). It was shown that $Fe_{78}Si_9B_{13}$ metallic glass had exceptionally high capability for activating these three common peroxides to produce reactive radicals ($\cdot OH$ and/or $SO_4{}^{\bullet -}$). The dominant species of H_2O_2 in this work was demonstrated as hydroxyl radical ($\cdot OH$) while the PS and PMS activation mainly generated sulfate radical ($SO_4{}^{\bullet -}$). The order of predominant radical generation rate by $Fe_{78}Si_9B_{13}$ activation under UV−vis irradiation was PS > H_2O_2 > PMS. The relative contribution of sulfate radical ($SO_4{}^{\bullet -}$) in PS activation was 78% compared to 61% in PMS. All the peroxides activated by $Fe_{78}Si_9B_{13}$ metallic glass presented a radical generation rate at least ~2 times higher than other iron-containing materials. Crystal violet (CV) dye was used to investigate the catalytic performance of $Fe_{78}Si_9B_{13}$ metallic glass for peroxides, which showed an ultrafast dye degradation rate with completely color removal within 15 min. The radical evolution mechanisms for H_2O_2, PS and PMS activation were also investigated. The change in surface morphology of ribbon after 5th run reused indicated that the inclusions of Si leading to formation of SiO_2 layer played an important role in the surface stability of ribbons.

1. Introduction

In addition to superior properties as structural materials, metallic glasses have been extensively studied to show a wide range of remarkable properties as functional materials, such as antibacterial ability in combination with plastics-like processability of Zr-based metallic glasses [1,2], superior thermal stability and good soft ferromagnetic property of Fe-based metallic glasses [3] as well as excellent biocompatibility and corrosion resistance of Ca/Ti-based metallic glasses [4,5]. In recent years, due to the advanced catalytic activity combined with other practical performances (e.g. excellent corrosion resistance property), various kinds of metallic glasses have been attracted more research attention in wastewater remediation. For example, MgZn-based amorphous powder exhibits a high degradation capability for direct blue 6 dye and 20 times faster degradation efficiency than its crystalline counterparts [6]; Al-based glassy ribbon presents a superior applicability in wide pH conditions with the degradation efficiency in the alkaline and acidic condition having 1.5 times and 189 times, respectively, faster than in the neutral pH [7]; Co-based amorphous powder shows that the surface-area-normalized rate constant is 3 orders of magnitude higher than the commercial iron powder, leading to a ultrafast degradation rate for acid orange II solution with at least 6 times of reusability [8]. Largely owing to the low cost, friendly environmental compatibility and sustainable property with easy recycling, Fe-based metallic glasses haven been emerging as the superior candidates in wastewater treatment. Different compositions of metal or metalloid have also been combined to study catalytic activity and reaction mechanism of Fe-based metallic glass. For

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Abbreviations: BA, Benzoic acid; CV, Crystal violet; DSC, Differential scanning calorimetry; EDS, Energy-dispersive X-ray spectroscopy; EtOH, Ethanol; PMS, Peroxymonosulfate; PS, Persulfate; SEM, Scanning electron microscope; TBA, Tert-butanol; TEM, Transmission electron microscopy; XRD, X-ray diffraction

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instance, recent reports demonstrate that $(Fe_{0.99}Mo_{0.01})_{78}Si_9B_{13}$ glassy ribbon can almost completely decolorize direct blue 2B dye solution in 30 min at the controlled temperature of 60 °C [9]; $Fe_{73}Si_7B_{17}Nb_3$ amorphous powder is able to remove direct blue 6 with 200 times higher reactivity than Fe powder [10]; $Fe_{76}B_{12}Si_9Y_3$ amorphous powder can rapidly degrade methyl orange dye with 13 times reusability [11]. Besides, nanocrystallized Fe-based glassy ribbons (e.g. $Fe_{82.65}Si_4B_{12}Cu_{1.35}$ [12], $(Fe_{73.5}Si_{13.5}B_9Nb_3Cu_1)_{91.5}Ni_{8.5}$ [13,14]) have been reported to show an unexpectedly higher efficiency than the amorphous counterpart as the formation of galvanic cells. However, all these reactions are mostly on the basis of direct transfer of electrons [8]. Direct reduction of dye solution by glassy ribbons usually cannot obtain desirable efficiency due to relatively lower specific area compared to amorphous powders. Although a higher degradation efficiency can be achieved by ball-milled amorphous powders owing to their higher specific area and strong residual stress [10], the ball-milling procedure is needed and the manufacturing cost is thereby increased. A long processing time (up to 50 h [11]) is also required for producing ball-milled powders from ribbons. Some endeavors have been made in order to enhance the degradation performance of glassy ribbons and facilitate the operation of wastewater treatment. Recently in our previous work, the additions of 1.0 mM hydrogen peroxide (H_2O_2) and 1.0 mM persulfate (PS) were reported to highly improve complete removal of methyl blue within 15 min and 20 min, respectively, when using $Fe_{78}Si_9B_{13}$ glassy ribbons as the Fenton-like/sulfate radical-based reagent [15–20], which are based on advanced oxidation processes (AOPs).

Very recently, AOPs including ozonation [21], photocatalysis [22–24], sulfate radical-based oxidation process [25–27], Fenton/Fenton-like process [19,20] have been extensively studied as promising techniques due to their high degradation efficiency and high mineralization rate on refractory pollutants in wastewater. These oxidation processes rely on the production of reactive species with high redox potential, such as hydroxyl radicals ($\cdot OH$, $E^0 = 2.7$ V [28]) and sulfate radicals ($SO_4{\bullet}^-$, $E^0 = 2.5\text{-}3.1$ V [29]), to completely convert organics into H_2O, CO_2 and harmless inorganic substances [16]. The $\cdot OH$ mostly originates from hydrogen peroxide (H_2O_2) in the Fenton/Fenton-like reaction whilst the persulfate (PS) and peroxymonosulfate (PMS) are used as donors of $SO_4{\bullet}^-$ in the sulfate radical-based system. Although these three peroxides have the high self-redox potentials (1.78 V for H_2O_2, 2.01 V for PS and 1.82 V for PMS) [30], their limited oxidation ability is still insufficient for organic compounds degradation. To improve the oxidation performance, iron salts are usually introduced to stimulate H_2O_2 to produce free radicals $\cdot OH$ in the conventional Fenton/Fenton-like process [20] while the ultraviolet (UV), heat and iron salts are favorable for $SO_4{\bullet}^-$ generation from PS or PMS in the sulfate radical-based oxidation process [25,26,30]. Apparently, iron ions play an important role in activating H_2O_2, PS and PMS. However, adopting iron salts as Fenton reagents has several main drawbacks as follows: (1) producing additional iron sludge when pH increases [18]; (2) giving rise to secondary contamination in excessive use of iron salts [31]; (3) difficulties in reusing iron salts [32]; and (4) increased cost for disposing iron sludge in industrial scale [32]. Recently, the iron containing solid compounds in Fenton-like/sulfate radical-based process are employed as an alternative strategy to overcome some of the aforementioned disadvantages. They can be classified into (1) iron oxides (e.g. α-Fe_2O_3 [33], γ-Fe_2O_3 [34], α-FeOOH [35] Fe^0/Fe_2O_3 [36]), (2) doped iron oxides (e.g. S/α-Fe_2O_3 [37], Nb/iron oxides [38], Cu-doped goethites [39]) and (3) iron oxides containing materials (e.g. magnetite [40], Bi_2WO_6/Fe_3O_4 [41], iron–cobalt mixed oxide [42]). Most of these iron-containing solid compounds present as powder form, which is hard to reuse (filtration and dryness are needed). The doped iron oxides and iron oxides containing materials require a series of synthesis and preparation procedures, e.g. separation of suspension from chemosynthesis before long-time dryness and calcination. On the other hand, although the iron oxides powder with the large specific surface area have a very strong adsorption ability and they can provide much more reactive sites for peroxides reaction and pollutants decomposition, the reactive performance of some iron oxides compounds, e.g. α-Fe_2O_3 [33], Fe^0/Fe_2O_3 [36], magnetite [40] iron–cobalt mixed oxide [42], in Fenton-like/sulfate radical-based reaction is somewhat bad, where more than 60 min of full removal of pollutants is needed. However, the FeSiB glassy ribbons do not require the costly surface modification and powder fabrication due to the high activation efficiency for peroxides. As the alternative Fenton reagents, Fe-based glassy ribbons have an outstanding activation efficiency for peroxides with low specific surface area and very low mass lose due to the uniquely atomic packing structure facilitating metallic glasses a lower activation energy for electron transfer, which extremely extends the active surface area and provides abundant active sites for redox reactions, thereby achieving a high catalytic reactivity [8,18]. Very recently, Fe-based glassy ribbons have demonstrated its superior reactivity in Fenton/Fenton-like and sulfate radical-based processes [15,20,43]. However, the activation behavior of Fe-based glassy ribbons on the common peroxides (H_2O_2, PS and PMS) has rarely been discussed and compared.

In this work, a comparative study of $Fe_{78}Si_9B_{13}$ glassy ribbon on the activation for H_2O_2, PS and PMS under photo-enhanced process is discussed. Further investigation of activation behavior of $Fe_{78}Si_9B_{13}$ glassy ribbon is based on the oxidative degradation of crystal violet (CV) dye using these three peroxides. The dominant radical evolution by $Fe_{78}Si_9B_{13}$ metallic glass is discussed and the functionality of atoms in the ribbons is also shown in detail.

2. Experimental

2.1. Materials and chemicals

The glassy ribbons with nominal composition of $Fe_{78}Si_9B_{13}$, which were cut into 5 mm wide and 20 mm long with a thickness of 30–40 μm, were manufactured by vacuum melt-spinning [44,45]. The master alloy ingot of $Fe_{78}Si_9B_{13}$ was firstly prepared by arc melting under a Ti-gettered argon atmosphere for 5 times to achieve homogenous chemical composition. From the master alloy, the glassy ribbons were fabricated by ejecting melting master alloy on a single copper roller with a wheel speed of about 30 m/s. The crystal violet (CV) dye was supplied by Wenzhou Huaqiao Chemical Reagent Co., Ltd., China. The benzoic acid (BA, ≥99.5%), oxone ($KHSO_5{\cdot}0.5KHSO_4{\cdot}0.5K_2SO_4$), vanadium oxide ($V_2O_5$, 98%), *tert*-butanol (TBA, ≥99%) were purchased from Sigma-Aldrich. Other chemicals including sodium persulfate ($Na_2S_2O_8$), hydrogen peroxide (H_2O_2, 30 wt.%), sodium nitrite ($NaNO_2$), sodium bicarbonate ($NaHCO_3$), potassium iodide (KI), sodium hydroxide (NaOH, 0.1 M), hydrochloric acid (HCl, 0.1 M), sulfuric acid (H_2SO_4, 0.5 M), ethanol (EtOH, absolute) and Milli−Q water (18.2 M Ω·cm) were all in the analytical grade without purification.

2.2. Characterizations

The structural features of the as-received $Fe_{78}Si_9B_{13}$ glassy ribbons were identified by X-ray diffraction (XRD) recorded on a PANalytical Empyrean diffractometer (Netherlands) with Co-Kα radiation at ambient temperature and transmission electron microscopy (TEM) using a JEOL JEM-2010 microscope (Tokyo, Japan). Differential scanning calorimetry (DSC, Netzsch 404C, Germany) at a heating rate of 20 K·min^{-1} was used to investigate the thermal physical parameters including Curie temperature (T_c) and onset crystallization temperature (T_x) for as-received $Fe_{78}Si_9B_{13}$ glassy ribbons. The surface topography and atomic composition before and after oxidative degradation were analyzed by a scanning electron microscope (SEM, JEOL JCM-6000Plus, USA) equipped with energy-dispersive X-ray spectroscopy (EDS) detector.